NOV 2, 1922

DEPARTMENT OF COMMERCE

CIRCULAR

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 80

PROTECTIVE METALLIC COATINGS FOR THE RUSTPROOFING OF IRON AND STEEL

[2d Edition]
SEPTEMBER 2, 1922

PRICE, 20 CENTS
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PROTECTIVE METALLIC COATINGS FOR USE AUSTENITIC OR HIGH ALLOY STEEL

ISSUED JUNE 1, 1920

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PROTECTIVE METALLIC COATINGS FOR THE RUSTPROOFING OF IRON AND STEEL.

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I. INTRODUCTION.

1. NATURE OF CORROSION.

Various theories have been advanced concerning the nature of the process of the corrosion of iron and a vast amount of experimental work has been done to support these theories. All agree, however, that, at least in part, the process is electrolytic in its nature and the various hypotheses differ mainly as to the factors by which the electrolytic action is brought about. Iron and steel will not corrode in dry air, the presence of moisture is an essential condition, and, according to one of the theories, carbon dioxide must also be present. Protection from atmospheric corrosion may be afforded in two ways, first, by mechanically excluding all moisture and other corroding agents from the iron and steel; and second, by using coatings of such a chemical nature that the covering itself is corroded in preference to the iron or steel beneath. It must be remembered that all rustproofing processes are temporary only in character; some, however, are so far superior to others that the use of the term "rustproofed" is justifiable in such cases.

The attempt to prolong the life of iron and steel parts in service by protecting them against corrosion has led to the adoption of many materials and processes for coating. The protective materials fall in general into three classes, (*a*) the metallic coatings, (*b*) the coatings in which the iron to be protected is itself converted at the surface into some less corrodible compound, and (*c*) the organic coatings, including paints, varnishes, enamels, etc. The metallic coatings include all the common metals and alloys that can be applied at all readily to steel, namely, zinc and aluminum, which are electronegative to iron,[1] and tin, lead, terne and other lead alloys, copper, nickel, cobalt, brass, bronze, and silver, all of which are electropositive to iron. In the case of the iron compounds, the iron at the surface is converted to oxide, or to some other compound, and the piece is then usually given an oil finish. The organic coatings will not be discussed in this circular.

2. PRINCIPLES UNDERLYING METHODS OF PREVENTION OF CORROSION.

Of the metallic coatings, by far the best for general rustproofing is zinc. The principal reason for this lies in the chemical nature of zinc. It is the only one of the commonly used metals that is electronegative to iron—that is, it has a greater tendency to be

[1] The signs used in this Circular to express the potentials of electrodes are in conformity to the official recommendation of the American Electrochemical Soc. Trans., 36, pp. 3–15; 1919.

oxidized than has iron. In the following list the metallic elements are arranged in their proper order in the potential series. Any element is electro negative to any element following and electropositive to any element preceding it in the list.

K..... Potassium.	Cd..... Cadmium.	As..... Arsenic.
Na..... Sodium.	Fe..... Iron.	Bi..... Bismuth.
Ba..... Barium.	Tl..... Thallium.	Sb..... Antimony.
Sr..... Strontium.	Co..... Cobalt.	Hg..... Mercury.
Ca..... Calcium.	Ni..... Nickel.	Ag..... Silver.
Mg..... Magnesium.	Sn..... Tin.	Pt..... Platinum.
Al..... Aluminum.	Pb..... Lead.	Au..... Gold.
Mn..... Manganese.	H..... Hydrogen.	
Zn..... Zinc.	Cu..... Copper.	

When any steel article with a metallic coating is scratched or abraded so that a small area of the steel is exposed, the two dissimilar metals, together with a small amount of moisture derived from the atmosphere, will form a tiny galvanic cell, set up a current, and start corrosion. That metal which is electronegative to the other will be the one to be oxidized, while the electropositive metal will remain uncorroded. Therefore, if the coating metal is zinc, it is zinc that will be oxidized, while the iron remains bright and uncorroded until the bare spot becomes so large that the central portion is beyond the protective zone of the surrounding zinc. On the other hand, should the coating happen to be tin, which is electropositive to iron, it would be the steel that would suffer. In such a case the tin coating is actually injurious, because without it the steel would oxidize at the normal rate with no galvanic action to hasten the corrosion. The value of tin for coatings depends upon other factors than its electrochemical nature.

Zinc, then, has the advantage of being electronegative to iron and so prevents its corrosion, especially on small exposed areas, such as "pinholes" in the coating, scratches, etc. One other common metal, aluminum, is also electronegative to iron, but does not share the other advantages enjoyed by zinc, such as relatively low cost, the ease with which it can be applied to steel in quite a number of ways, and the fact that with a little care it will solder readily (1 to 11, inclusive).[2]

[2] Numbers in parentheses which appear throughout this paper refer to the Bibliography, pp. 32 to 34.

II. TYPES OF COATINGS AND METHODS OF APPLICATION.

1. METALLIC COATINGS.

(*a*) ZINC.—The oldest process for zincing or galvanizing, and the one most widely used, is the hot-dipping process, in which the steel after a preliminary cleaning of the surface is immersed in molten zinc, left in the bath long enough for the steel to reach the temperature of the zinc, and then withdrawn with the coating of zinc adhering to it (24, 25, 26, 27). It is a simple process and gives excellent results on smooth surfaces.

Another method of zincing, called "sherardizing," consists in heating the steel in a so-called zinc-vapor atmosphere. The steel parts are packed in a revolving drum with zinc dust containing a small amount of zinc oxide, and heated at 350° to 375° C. (28, 29, 30, 31, 32, 33, 34). The cylinder is made to rotate slowly on its axis, to tumble the parts and insure evenness of coating. Usually three and one-half to four hours heating are required to produce a satisfactory coating.

Zinc is also applied to steel by plating from an aqueous solution (36, 37, 38, 39, 40). Those commonly used are either a solution of zinc sulphate containing a small amount of free acid or a solution of zinc cyanide or one of zinc oxide in a mixture of sodium cyanide and sodium hydroxide. The plating usually takes from a half hour to an hour but may be continued longer to produce very heavy deposits.

There are other methods of applying zinc which are used less often. The Schoop spray gun, for example, is a device for spraying molten metal upon an article to be coated (41, 42, 43, 44). The zinc, in the form of wire, is fed into the spray gun where an oxyacetylene flame melts it and a strong current of air projects it from the nozzle in the form of a very fine spray, which is directed against the steel. In the most recent form of apparatus, the wire is fused by an electric arc. An investigation now in progress at the Bureau of Standards indicates that a very decided improvement of the deposited coating is obtained by spraying with a blast of some inert gas rather than with air. In another process called "epicassit," the zinc in the form of filings is mixed with a flux, made into a paste and then painted on the steel (45). The article is then heated until the zinc just melts, making a continuous adherent coating.

Of the three forms of zincing most commonly used, namely, hot dipping, sherardizing, and electroplating, each type has its

advantages and its disadvantages. Hot dipping is excellent for even surfaces, as it gives a heavy coating in a very short time. The thickness of coating on such material as sheets and wires can be easily regulated by wiping and other mechanical devices; on irregularly shaped articles, however, there is no simple way of regulating the amount of zinc used. This method can not be used on accurately machined parts, such as screw threads, for obviously the zinc would collect in sharp corners and alter the original outlines of the piece. Neither can it be used on a highly hardened steel where the heating to 450° C. (the approximate temperature of the zinc bath) would soften the steel too much for its intended use.

Sherardizing has the advantage of giving very even coatings. The coating on a screw thread, for example, will show no appreciable variation from the top to the root of the thread. On the other hand, sherardizing is a slower process, and it can not be used on such hardened steels as would be softened too much by heating at 375° C. for three or four hours. Neither is the method suited to handling large sheets, etc.

Electroplating has the advantage of being readily applied to small and delicate articles that are not easily handled in other ways, and the obvious advantage that it can be applied to steel without modifying any previous heat treatment. One advantage of this process is the ease of operation. There are several devices now upon the market by means of which the operation (including the preliminary cleaning and final washing) can be made a continuous one, requiring but little supervision. Another distinct advantage of electroplating is the ease of control of the thickness of the deposit, which within rather wide limits is directly proportional to the period of deposition. On parts having sharp corners or depressions, however, it is apt to give uneven coatings. On threads, for example, there will be an accumulation of zinc at the top of the thread, while the root may be nearly bare, and even on flat plates it has been found that the coating is heavier at the edges than in the center. It has been found, both in experiments at this bureau and elsewhere (40 a), that the cyanide plating solutions possess much better "throwing power" than the sulphate solutions and therefore lead to the production of more uniformly distributed deposits.

Cadmium, a metal which closely resembles zinc in its properties, is now being used commercially to a limited extent for electro-

plating iron and steel. It is claimed by the promoters of the process [3] to have some decided advantages over zinc for this purpose. Preliminary tests by this bureau seem to justify some of the claims made.

(*b*) ALUMINUM.—Aluminum has never been used commercially on a large scale for rustproofing, on account of the difficulty of applying it to steel. Aluminum is electronegative to iron and would, therefore, make a good protective coating. One method of applying it, called "calorising" (46, 47), is somewhat similar to sherardizing, in that the steel is packed in a mixture containing powdered aluminum and heated at 900° to 950° C. This process is used commercially to a considerable extent.

(*c*) SOFT FUSIBLE METALS (TIN, LEAD, AND THEIR ALLOYS).—Almost all of the metallic coatings other than zinc and aluminum divide naturally into two classes, the soft low-melting-point ones, and the hard metals with relatively high fusion points. Those in the easily fusible class, such as tin, lead, and their alloys, are applied almost altogether by hot dipping. Those not so readily fused, such as copper, nickel, cobalt, silver, brass, etc., are for the most part electroplated.

One of the most widely used of the coating metals is tin. It is in the class of metals that are electropositive to iron, so that a tin coating must be free from pinholes and must not be abraded or injured, or accelerated corrosion will set in where the steel base is exposed. However, the tin itself corrodes very slowly, and it has several advantages in that it is applied very easily by hot dipping, is soldered more readily than any other coating, and has the further very important advantage of having no toxic effect, so that it can be used in food containers. Hot dipping is used for the large majority of tinned articles, but the metal may also be applied by the Schoop spray and by plating (51, 52, 53).

Lead alloys are applied by quite the same processes as is tin, but they lack some of the advantages of tin. Lead does not solder so readily because it oxidizes quickly when heated, but it is much cheaper than tin, and has been used especially in terne, which is an alloy of about three-fourths lead and one-fourth tin. The electrodeposition of lead for the production of protective coatings has recently come into commercial use. Lead, however, is electropositive to iron and has the corresponding defects (54).

[3] Udilite process.

(*d*) HARD METALS (COPPER, NICKEL, COBALT, AND BRASS).—Copper has been used a great deal for rustproofing. Metallic copper itself corrodes very slowly, and it has found such wide application largely because it is applied very readily by electroplating. But it is electropositive to iron, so the coating must be well applied and be free from bare spots and pinholes to protect completely against corrosion. A practice that is fairly common is the buffing of coppered parts to give a bright finish. This renders the coating more uniform in thickness and covers up such imperfections as pinholes, etc. If the coating as deposited is very thin, however, severe buffing will remove it almost entirely in places and so accelerate corrosion.

In addition to electroplating, copper is applied with the Schoop spray gun, and by the so-called "copper-clad" process (49, 50). In the latter, copper is cast around a steel billet and the billet rolled down to rod or sheet form. Copper so applied is less likely to be porous than is the case with electroplated or sprayed metal. The process of depositing zinc coatings, designated as epicassit, has been modified for use in copper plating. The process is now being used industrially to a very limited extent (48).

Nickel is used for articles that are to have a light color, especially if a bright polish is desired. Most nickel is applied by electroplating, but it can also be applied by a process similar to the copper-clad process. Nickel is another one of the elements electropositive to iron. Since it is quite close to iron in the electrochemical scale, its injurious effect is likely to be a little less pronounced, however.

Cobalt is quite similar to nickel in its properties, and is used in much the same way.

The electrodeposition of brass upon steel can be carried out with success and is used extensively on small articles, such as builders' hardware, lighting fixtures, etc. It is plated from a solution containing both copper and zinc. It has no peculiar advantages as regards rustproofing, but the brass color is sometimes desired. Brass has also been applied as in copper-clad and nickel-clad products, as has also bronze.

2. OXIDES AND SALTS OF IRON.

(*a*) OXIDES.—The oxide coatings on iron and steel are in general prepared by heating the metal in a suitable atmosphere or by oxidizing in the presence of certain aqueous or fused

chemical reagents. Repeated alternate heatings in oxidizing and reducing gases give a comparatively heavy coating of black iron oxide, considered to be Fe_3O_4. The etching and coloring processes (55) give thinner coatings, usually of a lower order of resistance to corrosion. The oxide coatings are always oiled, and undoubtedly owe some of their rust resistance to this fact only (56).

Bower-Barff type.—The original Bower-Barff method consisted in heating the steel at 350° C. and above, in air or sometimes in the presence of superheated steam. When a coating of ferric oxide had been formed hydrocarbons were introduced which served to reduce the ferric oxide, Fe_2O_3, to ferroso-ferric oxide, Fe_3O_4. This process and the variations of it give a coating which offers a very fair degree of resistance to corrosion. One modern variation which is used extensively consists in heating at a low, red heat, in a mixture of steam and benzine. The modifications of the Bower-Barff process are known under quite a number of names, e. g., the Swann, the Bontempi (58), the Gesner, the Weigelin, etc.

Heating with oil, etc.—In this type of process the steel is heated in volatilized oil or in a thick smoky atmosphere, whereby a deep-black oxide coating is produced. The Carbonia process is typical, in which the steel is heated at about 220° C. in a mixture of burnt bone and oil. In other processes the steel is heated in burnt bone and charcoal, or in oil and sawdust. The steel may also be oiled first and then heated to a temperature ranging from 300° to 550° C. The process of blacking in a forge is similar: The steel is cleaned of loosely adherent scale and then held while quite hot in the thick, smoky flame from the forge.

Etching ("browning," "bluing," etc.).—Solutions of chemical reagents are applied to the steel with a cloth or sponge; the steel is allowed to oxidize for some hours while drying; the rust is then scraped off, leaving a thin adherent coat of oxide. The process is repeated a number of times, depending on the depth of color desired. The surface is then oiled. The following is a representative list of combinations of reagents that have been used for producing the respective colors:

Color, and reagent for producing.	Parts, by weight.
Black:	
First formula—	
Bismuth chloride	20
Mercuric chloride	40
Copper chloride	20
Hydrochloric acid	120
Alcohol	100
Water	1000
Second formula—	
Copper-nitrate solution (10 per cent)	700
Alcohol	300
Third formula—	
Mercuric chloride	50
Ammonium chloride	50
Water	1000
Brown:	
First formula—	
Alcohol	45
Iron-chloride solution	45
Mercuric chloride	45
Sweet spirits of niter (ethyl nitrite+alcohol)	45
Brown—Continued.	
First formula—Continued.	
Copper sulphate	30
Nitric acid	22
Water	1000
Second formula—	
Nitric acid	70
Alcohol	140
Copper sulphate	280
Iron filings	10
Water	1000
Blue:	
Iron chloride	400
Antimony chloride	400
Gallic acid	200
Water	1000
Bronze:	
Manganese-nitrate solution (10 per cent)	700
Alcohol	300

Niter bath.—The cleaned steel is heated in fused sodium nitrate or potassium nitrate or a mixture of the two, often with the addition of manganese dioxide. The color acquired by the steel depends on the temperature of the bath, as well as its composition. Other fused oxidizing baths can probably be used also.

Temper colors.—The "temper colors" seen on steel when it is heated between 220° and 320° C. are due to a thin layer of oxide. Such a layer of oxide is often applied as a protecting coating, the blue color being the one usually used. The steel is heated in free air and the various colors will be produced at the following temperatures:

Temper color.	° C.	° F.	Temper color.	° C.	° F.
Pale yellow	220	418	Purple	280	536
Straw	230	446	Pale blue	300	572
Brown	255	491	Dark blue	315	599

The color depends somewhat on the duration of the heating and to a lesser extent on the nature of the steel.

Hot oxidizing solutions.—Boiling alkaline oxidizing solutions have been used, such as boiling sodium-hydroxide solution, containing sodium picrate (Guerini process), sodium nitrate, sodium peroxide, etc. It seems probable that many oxidizing solutions would be found suitable. The nature of the steel affects the structure of the coating produced.

Miscellaneous.—Other processes for producing black coatings include the following: Immersion in boiling solution of lead ace-

tate and sodium hyposulphite; making the iron the anode in an electrolytic cell, the oxygen from the decomposition of the water giving a coating of oxide; dipping in 10 per cent potassium-bichromate solution, followed by heating in a smoky flame; copper plating by dipping in copper-sulphate solution, followed by immersion in a solution of sodium hyposulphite and hydrochloric acid. A brown color may be produced by heating in steam with acid vapor for a few hours. A type of coating termed "black nickel" is used rather extensively. This is electrolytically deposited, but the commercial practice varies widely as to the composition of the bath used and hence also the coating (59a). The deposit made from the sulphocyanate bath is most uniform in its composition and properties and is to be preferred, particularly if the article has received a preliminary coating of zinc.

(*b*) SALTS.—In a coating of this type of rather wide commercial application, the iron at the surface is converted into a salt by immersing the steel in hot dilute phosphoric acid, sometimes containing manganese dioxide, soluble chromates, or other metallic salts. After the proper length of immersion, the steel is withdrawn and dried. The color is then grayish-white, but becomes black when oiled. This is called the Parker (57) or the Coslett process (59). Its resistance to corrosion is of the order of the light oxide coatings. (See also p. 31.)

III. MICROSTRUCTURE.

Most of the metals used for covering iron and steel as a preventive of corrosion form coatings which are very simple in structure. The metal alloys with the iron of the base to such a slight extent that no change in the microstructure of the resulting coating can be detected and, in all probability, the behavior of the coating in resisting corrosion is not affected to an appreciable extent. With zinc, however, the case is quite different (15, 16, 18, 21, 23); particularly is this so in the coatings which are made by the application of heat. The zinc alloys with the iron to such a degree that the coating is relatively complex in structure and the properties of such coatings are very appreciably affected. In some coatings (52) certain of the microstructural constituents present may actually accelerate the attack of the metal which the coating is aimed to protect, and the technical literature contains various misleading statements (21) which, if correct, would suggest that a similar condition may exist in certain classes of zinc coatings.

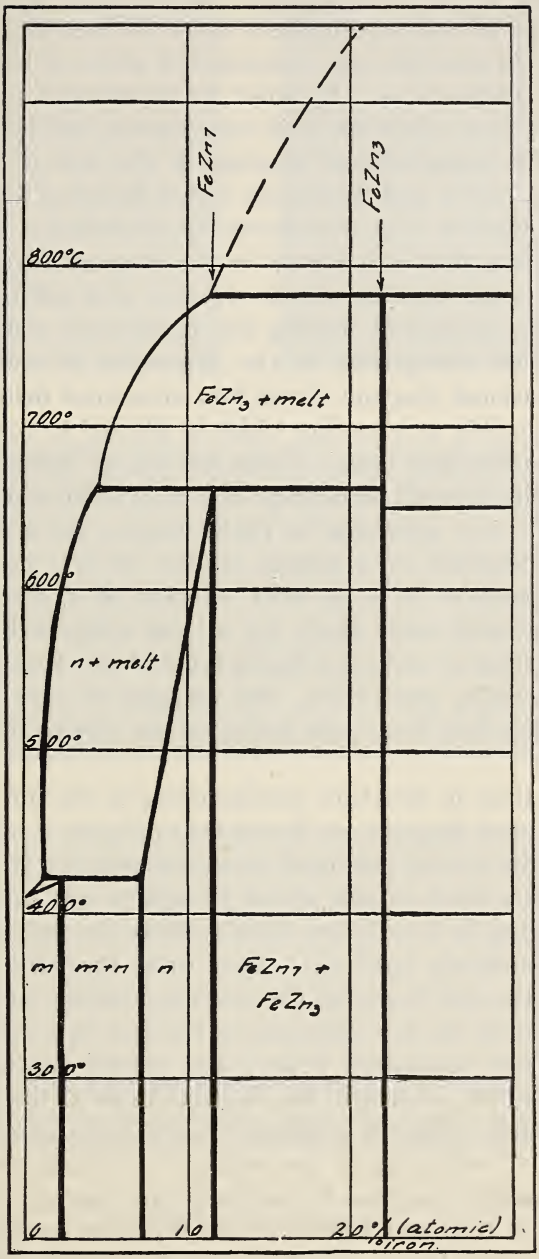


FIG. 1.—*Portion of the constitutional diagram of the zinc-iron alloys.*

1. THEORETICAL MICROSTRUCTURE OF ZINC COATINGS.

In at least two of the four types the coating is far from being a simple layer of zinc superimposed upon the base metal beneath, but is a rather complex one, composed of alloys of iron and zinc of various compositions. In order to understand properly the formation of these alloys and their composition, and for purpose of reference, the constitutional diagram of the iron-zinc alloys as modified by Raydt and Tammann (17) is included herewith. A recent investigation (23a) has shown the solubility of iron in zinc to be much less than is indicated in the diagram Figure 1.

Alloys of more than 25 atomic per cent iron are formed only with difficulty, usually by melting the constituents under pressure, hence may be disregarded in the discussion of zinc coatings. The constitutional diagram shows four structural fields or layers which are possible in a coating which is allowed to come to equilibrium with the iron base. These are (1) an outer one, *m*, of zinc containing a small percentage of iron in solid solution (about 0.7 per cent; 0.02 according to Pierce (23a)); (2) a duplex one, *m* . . . . *n*, composed of a matrix similar to (1), in which are embedded particles of *n* (a solid solution of a chemical compound $FeZn^4$ with some zinc); (3) a layer composed entirely of the solid solution *n;* and (4) a duplex layer of two definite chemical compounds $FeZn_7$ and $FeZn_3$, the amount of each compound varying in this field from pure $FeZn_7$ on one side to $FeZn_3$ on the other.

The variations in structure corresponding to the different fields of the structural diagram are illustrated in Figure 2, which shows portions of the coating produced on an iron wire (16 B. & S. gage) embedded in a block of zinc about ⅜ inch (1 cm) square in section by heating for four hours slightly above the melting point of zinc (approximately 450° C.). Iron from the wire permeated throughout the zinc block, so the resulting coating includes practically the entire block. Adjacent to the iron is a thin layer, *B*, of intermetallic compound $FeZn_3$; just outside of this a much thicker layer, *B'*, in which the definite form of the crystals is plainly seen (this probably contains both $FeZn_3$ and $FeZn_7$), a very thick layer, *C*, consisting of tiny crystals of the compound $FeZn_7$ in a softer matrix comprises by far the greater part of the coating; the crystals in the outer margin of this layer are particularly well formed and much larger than the average throughout the layer. The outermost portion, *D*, of the coating shows the characteristic

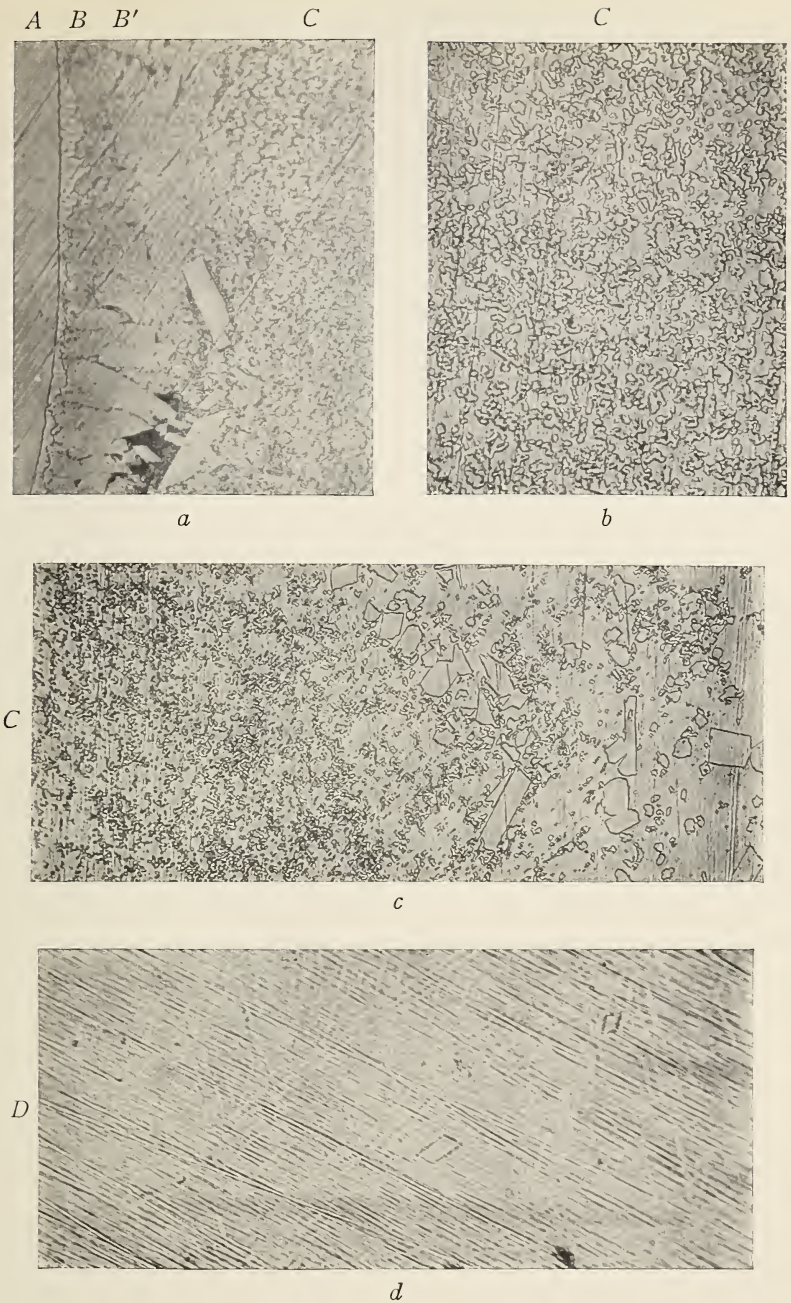
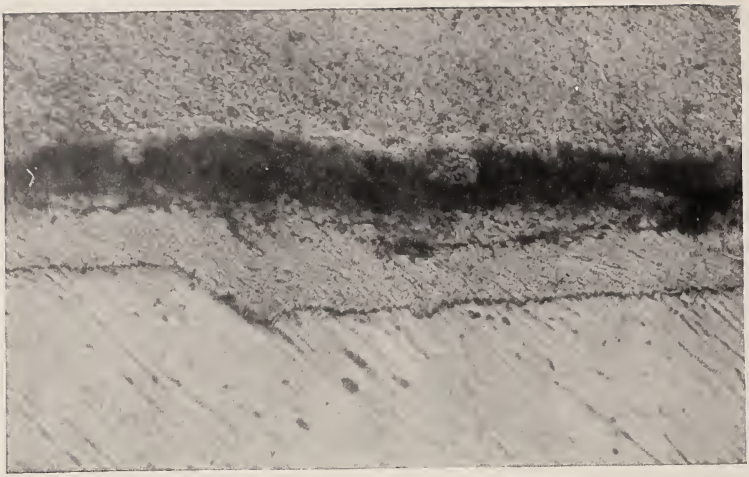


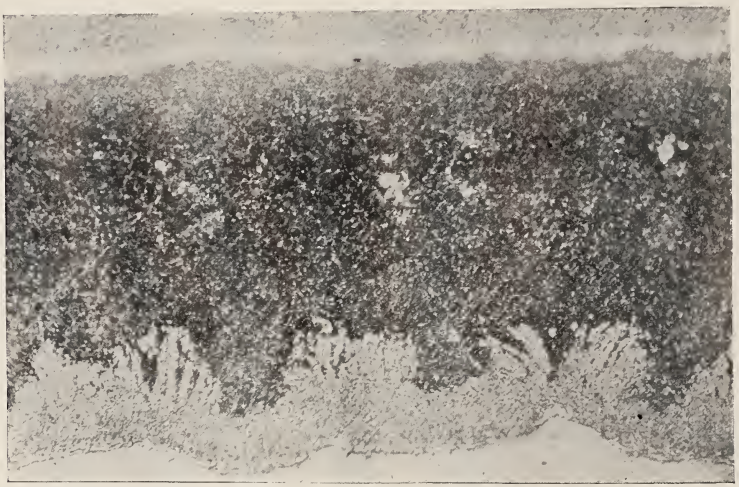
FIG. 2.—*Microstructure of zinc coating formed on an iron wire immersed in molten zinc for four hours*

a *A*=Iron wire.
B=Alloy layer $FeZn_3$, adjacent to the steel base.
B′=Layer of the compound $FeZn_7$ (with perhaps some $FeZn_3$).
C=Duplex layer of crystals of $FeZn_7$ embedded in a softer matrix of zinc containing some iron in solution. Magnification, 500 diameters.
b=Intermediate portion of layer C. Magnification, 500 diameters.
c=Outer portion of layer C. The crystals of $FeZn_7$ in the outer portion are large and well formed. Magnification, 200 diameters.
d=Outer layer of zinc (containing some iron in solution). The shadowlike etch markings are rather characteristic of zinc. Magnification, 200 diameters.

Etching: 1 per cent iodine in alcohol was used here and for the remaining samples, in following figures, unless stated otherwise.



a



b

FIG. 3.—*Commercial hot-dipped zinc coated sheets*

a=Thin coating; average weight of coating as determined by weighing the sheet before and after dipping, 1.37 ounces per square foot.

b=Thick coating; average weight, 2.5 ounces per square foot. The different layers have been lettered to correspond with those of Fig. 2. Magnification, 500 diameters.

All micrographs are arranged (here and following figures) so that the alloy, or inner layer, is toward the bottom of the page.

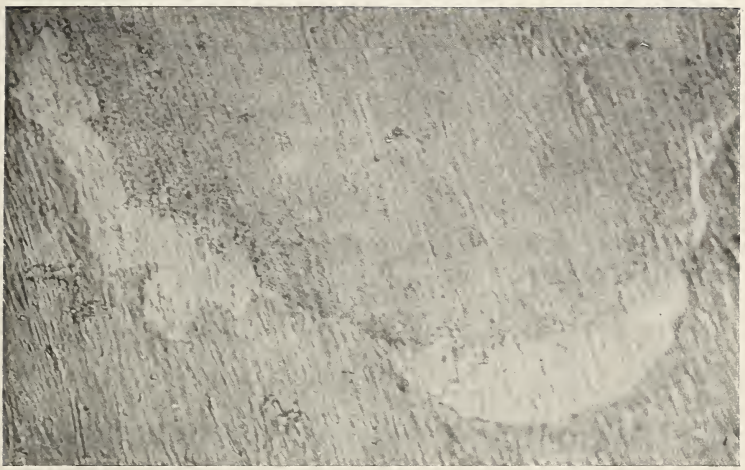
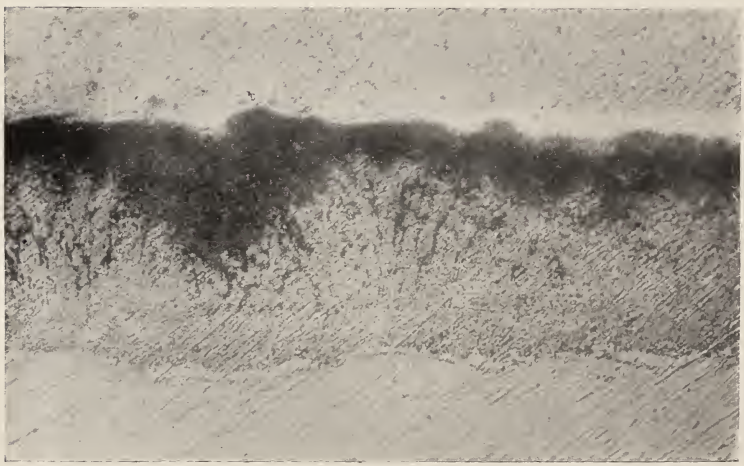


FIG. 4.—*Commercial hot-dipped zinc-coated sheets*

Oblique section of material of *b*, Fig. 3, showing the inner layers of $FeZn_3$ (white). Magnification, 500 diameters.

a



b

FIG. 5.—*Commercial hot-dipped zinc-coated sheets*

These were produced under unusual conditions.

a=Material similar to that of Fig. 3, which was held stationary in the molten bath for two minutes.

b=Material similar to *a* rerun through the molten bath four times.

The different layers have been lettered to correspond with those in Fig. 2.

The alloy layers have been much accentuated by these treatments. Magnification, 500 diameters.

etch markings of pure zinc; the metal here shows only a few traces of the second constituent; it undoubtedly contains iron in solid solution up to its saturation point (0.7 per cent). The nature of the various layers and their behavior during corrosion is discussed below.

2. VARIATIONS IN MICROSTRUCTURE OF COMMERCIAL COATINGS.

(*a*) HOT-DIPPED MATERIALS.—The variations in structure of this type of coating which may arise in practice are best shown by comparison with the structure when equilibrium is reached, as described above. In general the same layers are formed in specimens of this type; the relative amount of each constituent, however, varies considerably according to the conditions of dipping. Figure 3*a* shows the structure of a thin coating of this type (galvanized sheet, described by manufacturers as having 1.37 ounces of zinc per square foot; that is, 0.68 ounce per square foot on each side). A very thin innermost layer, *b*, of $FeZn_3$, is to be seen of approximately the same thickness as in the heavy coating (fig. 3*b*) which contains 2.5 ounces of zinc per square foot (1.25 ounces per square foot each side). Inasmuch as the thickness of the commercial coating is ordinarily controlled mechanically by adjusting the height of the molten bath relative to the guiding rollers and not by increasing the period of immersion in the zinc, it is to be expected that such would be the case. Figure 4 shows this innermost layer in a very oblique section of a coating. By holding the article to be coated for a much longer period in the molten zinc, this layer is given a chance to increase considerably in thickness, as is shown in Figure 5, *a* and *b*, which represents a sample held for approximately eight times as long in the bath as is considered good commercial practice, and a sample which was run through the bath several times in succession. The intermediate alloy layer, *c*, appears to be of approximately the same thickness in both the thinly and thickly coated commercial sheets, the difference in the weight of the coating being due to an increase of the outer zinc-rich layers in the thicker coating. The removal of the excess outer zinc-rich layer, *d*, in the thin coatings does not allow the crystals of the intermediate alloy layer, *c*, to form as perfectly as is the case in the thick coatings. By lengthening the time the molten zinc is in contact with the iron base the relative thickness of the alloy layers, *b* and *c*, is increased. This will be accompanied by a corresponding decrease in the outer zinc-rich layers, particularly in the coatings of sheets and wires,

in which the thickness is kept fairly uniform by some mechanical means. The significance of these alloy layers in service is indicated below (sec. 3). The sheets which were held for a considerable length of time in the molten zinc were found, after standing about two weeks, to be spotted with numerous exudations (fig. 6*b*). There is nothing in the microstructure to account for this other than some tiny pockets which were apparently filled with inclusions of the zinc and ammonium-chloride flux from the bath and which, under the influence of atmospheric moisture, swelled and exuded out of the coatings. Whether such inclusions of the flux will materially affect the life in service of such coated sheets can not be stated with certainty from a study of the structure alone. Most of the pits and inclusions, however, appear to be in the outer layers of the coatings, and not between the base metal and the coating.

(*b*) SHERARDIZED COATINGS.—In coatings of this type it is only in those of considerable thickness that any definiteness of structure appears. Figures 7 and 8 show the structural features which may be expected to occur in coatings of this type. The nature and composition of zinc-dust mixtures in which the articles are packed for heating probably determines almost entirely the nature of the outer layer. In the innermost layers alloying with the iron base occurs. The outer portions have a characteristic rough and porous appearance and contain a considerable number of inclusions of oxide and any foreign ingredients which may be present in the heated mixture. The inner portion of this outer layer is much denser than that near the outer surface and has a very characteristic appearance, being broken up by many fine intersecting cracks, caused probably by contraction upon cooling. The layer probably contains a considerable amount of the compound $FeZn_7$. The intermediate layer (fig. 8*b*), which easily etches dark, in all probability marks the outer limit of the pronounced alloying of the iron of the base with the zinc of the coating. An extremely thin layer immediately adjacent to the iron base, and apparently of the compound $FeZn_3$ marks the union of the coating with the base metal. In no coating except very thick ones (e. g., 0.008 inch) are these two innermost layers usually found; when much thinner (e. g., 0.002 inch or 0.0015 inch) the coating consists entirely of what, in the thicker ones, constitutes the outer layer.

(*c*) SPRAYED COATINGS.—The variations noted in this type of coatings are of a mechanical origin, due to the nature of the

a

b

FIG. 6.—*Surface appearance of hot-dipped sheets. Natural size*

a=Usual appearance.

b=Appearance of the material of Fig. 5*b*. Upon standing the surface became covered with spots of flux which exuded from within the coating.

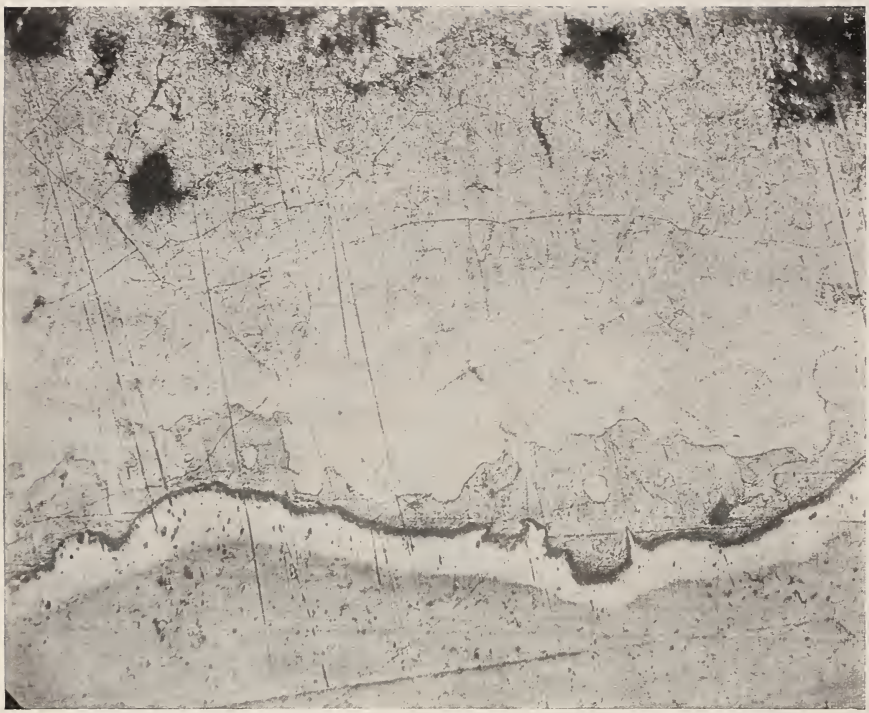
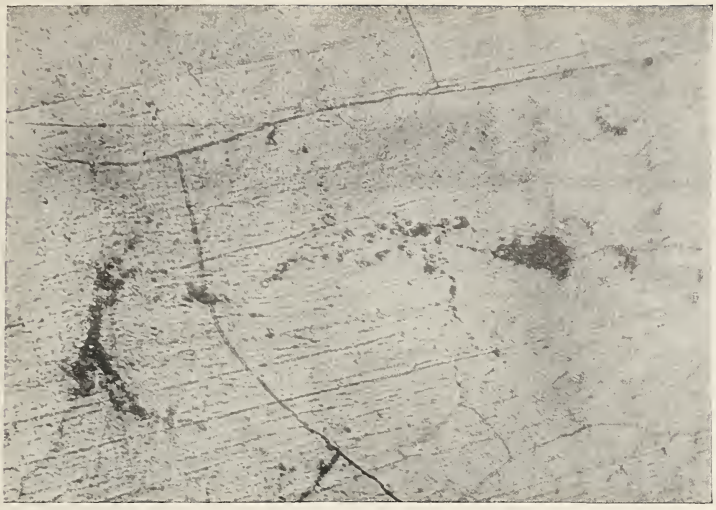
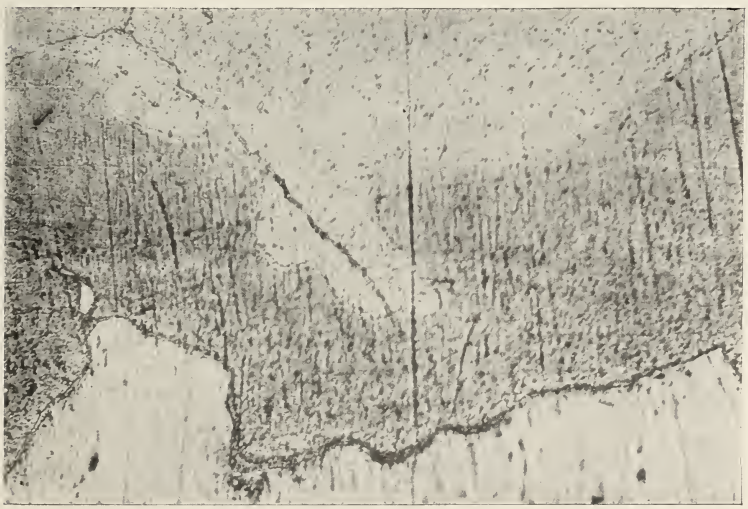


FIG. 7.—*Structure of sherardized coatings; oblique section of a coating averaging 0.008 inch in thickness. Magnification, 100 diameters*

a=Decarburized surface of the steel plate.
b=Inner layer of coating (probably contains $FeZn_3$).
c=Intermediate fissured layer of the coating ($FeZn_7$).
d=Roughened outer surface.



a



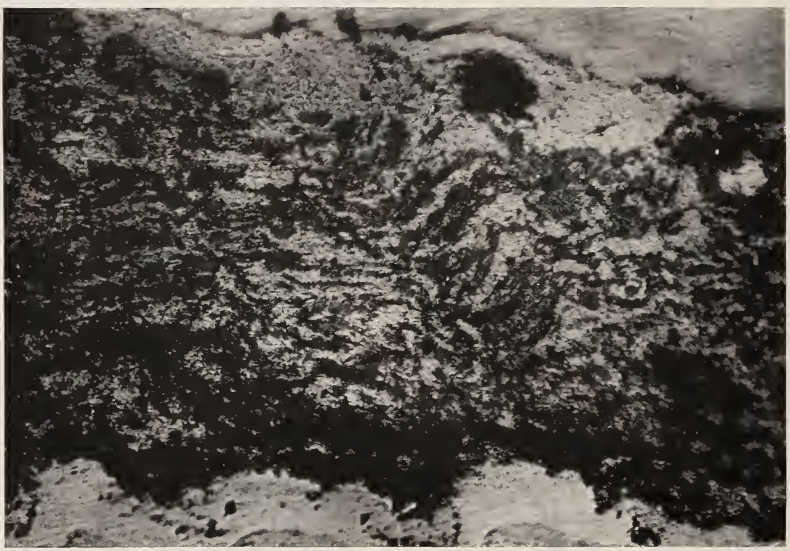
b

FIG. 8.—*Sherardized material. Magnification, 500 diameters*

a=Section of intermediate layer, showing the network of fine cracks and some of the inclusions retained from the heating mixture.

b=Inner layer, which probably represents the extent of the pronounced outward alloying action of the iron—a very thin film of the compound, presumably $FeZn_3$ lies immediately adjacent to the iron base.

a



b

FIG. 9.—*Cross section of sprayed zinc coating. Magnification, 500 diameters*

a=One-spray coat.
b=Four-spray coat.

method of deposition, rather than to any alloying of the zinc with the iron base. In Figure 9 are shown cross sections of two sheets coated by this process. The coating designated as "one spray" is very irregular and extremely thin in spots. The second sample was described by the manufacturers as a "four-spray" coat, but the structure suggests that a coating much heavier than this was applied. The distinct lamellæ which comprise the coat are due to the additional layers of zinc superimposed upon the earlier ones, with some accompanying oxide. Similar features are shown by sprayed coatings of other metals.

(*d*) PLATED ZINC COATINGS.—As is to be expected from the nature of the process by which such coatings are deposited, they are essentially of pure zinc and show none of the different alloy layers seen in the first two types. Figure 10 shows a coating of electrolytic zinc, deeply etched. No indications of structural variations across the section of the layer are to be seen. The principal point of interest in connection with the microstructure of this type is the variation in thickness which may exist on irregularly shaped pieces or even on flat surfaces. Such variations are to be found, particularly, in depressions and on sharp projections where the differences in the current density are considerable. This is especially true for the threaded portion of bolts and screws.

A set of measurements on two similar small machine bolts plated under identical conditions for different periods of time gave the following results:

Weight of coating computed from tank conditions.	Average thickness at top of thread.	Average thickness at root of thread.
Oz./sq. ft.	mm	mm
0.2	0.0157	0.0038
.55	.0224	.0053

Figure 11 shows the variation in thickness of coating on a small article having several sharp corners. The rivet is shown in natural size; the thickness of the coating has been magnified approximately 200 times. Even on flat surfaces the coating is not of uniform thickness. Figure 12 shows a series of thickness measurements made on sections of a plate 4 inches square which had been electroplated under very carefully controlled commercial

conditions. The sections were cut one-half inch apart, the longer one being taken along a diagonal of the plate. The plate is shown in natural size; the relative thickness of the coating has been magnified as indicated. The features described above for electrolytic zinc coatings may be taken as typical of coatings of other metals electrolytically deposited. The microstructure of electrodeposited coatings depends almost entirely upon the conditions of plating, composition, and concentration of solutions, etc. (14, 19). Figure 13 may be considered typical of a normal deposit of electrolytic copper from the commonly used acid-sulphate bath. The variations in thickness of such coatings in very deep, sharp grooves is shown in the same figure (fig. 13*b*). Figure 14 shows the structure of the copper-clad steel described in Section II–1–(*d*) above. A very thin but definite intermediate alloy layer has formed between the two metals.

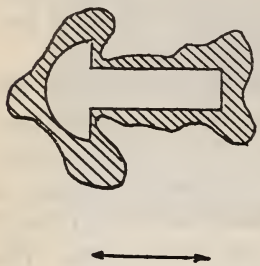


FIG. 11.—*Variation in thickness of a zinc coating deposited electrolytically upon an object having sharp angles.*

The rivet is shown natural size; the coating is magnified to the scale shown by the line, the length of which represents a thickness of coating of 0.07 mm.

3. SIGNIFICANCE OF STRUCTURE OF COATINGS.

Metallic coatings may protect the metal which they cover in different ways; all coatings afford a mechanical protection against moisture and other corroding agencies. Some metal coatings also by their greater solubility than the base metal protect the metal beneath from corrosion in a chemical way. As previously stated, of the common metals used for coatings, zinc is the only one which behaves in this manner. The significance of the various structures which may occur in different types of coatings should be considered with reference to the bearing they may have upon these two functions which the coating has to perform.

Various conflicting statements have appeared in the literature concerning the relative electrolytic solution potentials of the different zinc-iron alloys, particularly those which occur in galvanized coatings. The behavior of the alloy layers upon etching indicates that they are electropositive toward the zinc; that is, they bear the same general relation to zinc in this respect that iron does. More than this can not be stated with certainty from an examination of the microstructure alone. Guertler (21) states that the innermost layer ($FeZn_3$) is also more electropositive

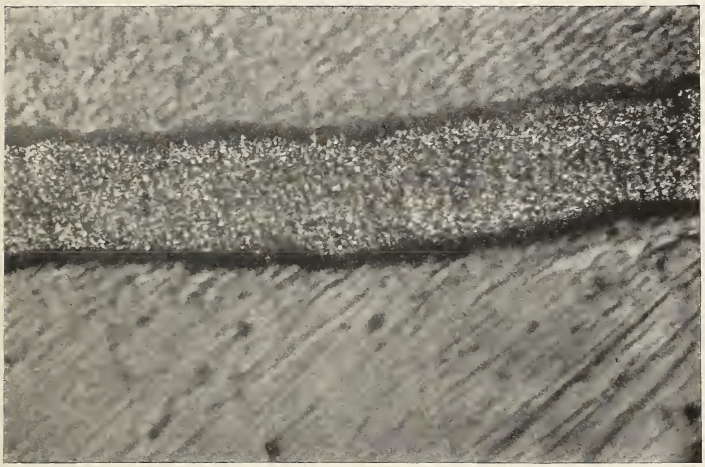


FIG. 10.—*Cross section of electrolytic zinc coating, deeply etched with 10 per cent sodium hydroxide. Magnification, 500 diameters*

FIG. 13.—*Electrolytic copper deposits*

a=Cross section of a deposit on a flat surface, plated from a sulphuric acid-copper sulphate bath with a relatively low current density.

b=Same type of deposit within a narrow v groove.

The arrow indicates the side from which the metal was deposited. Magnification, 150 diameters.

Etching: Concentrated ammonium hydroxide and hydrogen peroxide.

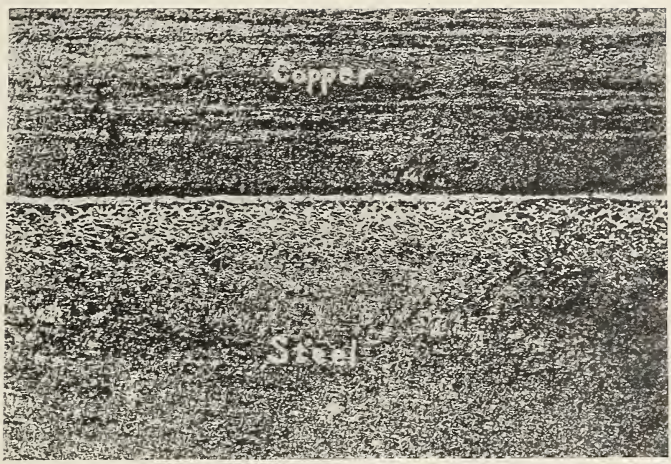
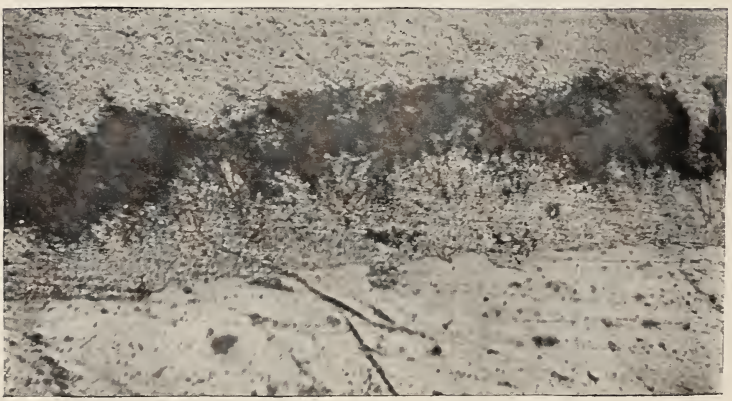


FIG. 14.—*Copper-clad steel*

A definite alloy layer has formed between the two metals. Magnification, 100 diameters. Etched with concentrated ammonium hydroxide followed by a 2 per cent nitric acid.

a



b

FIG. 16.—*Structure of hot-dipped sheet which stood more than 30 years' service*

a=Coating from the inner or unexposed surface.
b=Coating from the outer or exposed surface.
The different layers have been lettered to correspond with Fig. 2. Magnification, 500 diameters.

to the zinc than is iron, and hence iron will be electronegative to such a layer, so that when both are exposed to the corroding influences, by the wearing away of the outer layers by mechanical injury, etc., corrosion of the iron will be accelerated by the inner layers. Others have apparently reiterated Guertler's statement, though some have later corrected such statements. The diagram below is constructed from the emf measurements of the system $Zn - \frac{N}{20} ZnSO_4 - Fe$: Zn alloys (20) and shows that all of the alloys behave toward iron in the same general manner that pure zinc does, though not to the same degree. The ordinates of the curve show the value of the emf developed when zinc and the iron-zinc

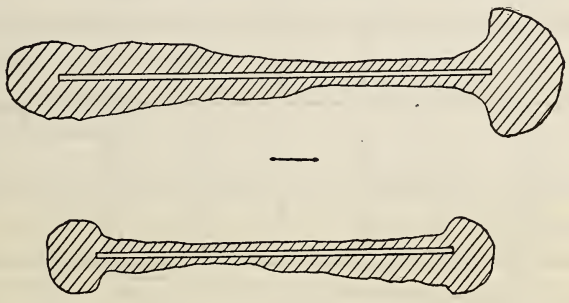


FIG. 12.—*Variation in thickness of a zinc coating (electrolytic) such as may occur on flat sheets after plating.*

The cross-hatched portion represents the coating drawn to the scale shown by the line the length of which represents a thickness of 0.094 mm. The cross sections of the sheet metal are shown approximately ½ natural size; the longer one was taken along a diagonal of the plate, the shorter one was a parallel section ½ inch away.

alloy indicated by the corresponding abscissa are made the electrodes within a solution of zinc sulphate.

Although both of the compounds, $FeZn_7$ and $FeZn_3$, are electropositive toward zinc, and so will aid in the solution of the zinc when either one is exposed to the corroding agency along with the zinc, it appears that such action is not serious and may safely be disregarded. Figure 16 shows a section of the coating on a hot-dipped galvanized sheet on the exposed and unexposed sides after more than 30 years of service.

The intermediate alloy layer in this material was remarkably well developed. The section of the exposed surface shows that the coating has been quite uniformly corroded away, and at the point where the section was taken the inner stratum of the alloy layer still remained intact. The claim has been made that zinc coatings containing as large a percentage of the alloy layer as consistent with the mechanical properties desired (freedom from

flaking on bending, etc.) are very desirable (35). On account of the lower potential difference between iron and the zinc-iron alloys, as compared with that between iron and the pure zinc, those coatings containing the excess of the alloys might be expected to have the longer life in service. Such coatings, however, will not be able to exert protective influence over as large bare spots as will those of much purer zinc.

Inasmuch as these alloy layers are never found in two of the other types, the sprayed and the electrodeposited, the resistance to corrosion of articles covered with such coatings depends en-

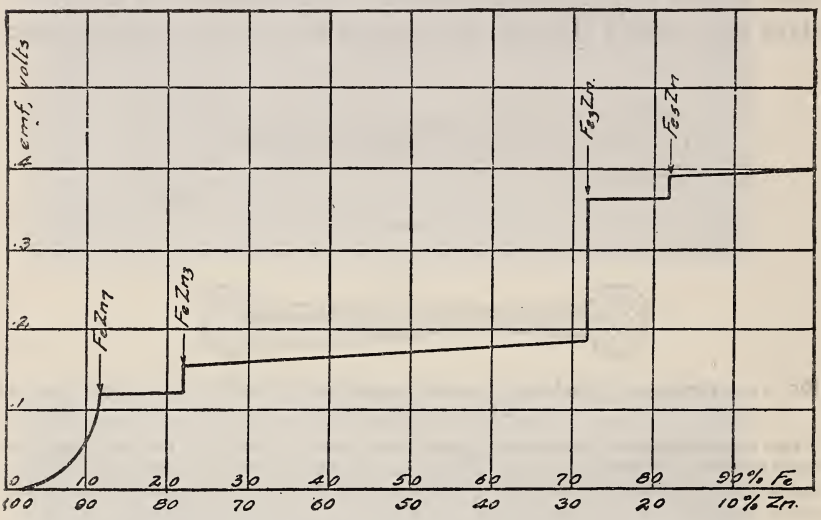


FIG. 15.—*Emf measurements of the system* $Zn-\frac{N}{20}ZnSo_4-Fe$: *Zn alloys.*

tirely upon the thickness of such coatings and to the uniformity of the coating. The variations which may be expected in this feature of these two types of coatings have been discussed above.

Like most intermetallic compounds, the layers of $FeZn_7$ and $FeZn_3$ are relatively hard and brittle. The compound $FeZn_3$ appears to be considerably harder than is the other compound, so that coatings in which it is well developed are easily separated from the base metal by sharp bending. The fine crystalline condition of the electrolytic and the sprayed coatings probably exerts as great an influence as does the absence of any brittle layers in such coatings in preventing them from stripping loose from the base metal, as is the case in thick coatings of the hot-dipped type.

IV. PREPARATION OF THE SURFACE BEFORE COATING, AND ACCOMPANYING EFFECTS UPON THE MECHANICAL PROPERTIES OF STEEL.

The successful application of coatings to steel requires that the surface of the specimen shall be clean; that is, free from all oxide and nonmetallic material. The general methods of cleaning are: The chemical (63, 64), in which the scale is removed by a direct chemical process of solution; the electrolytic (62, 66), in which the material is made anode or cathode in an electrolytic bath; and the mechanical, in which the scale is removed by abrasion, such as sand blast, tumbling, etc.

The most widely used cleaning process is a chemical one; it is the process of "pickling" in sulphuric acid. It has the advantages of being rapid and inexpensive, of reaching all parts of irregular specimens, and of being readily handled by inexperienced operators. In general the samples are immersed for from 5 to 30 minutes in sulphuric acid of concentration 2 to 15 per cent by weight, and at temperatures from 25 to 60° C. Other reagents for pickling include hydrochloric acid, hydrofluoric acid (which is especially useful for cleaning sand castings), and solutions of sodium-acid sulphate.

The chief disadvantages of pickling processes are (1) that when the thickness of the scale is not uniform over a specimen, the steel at cleaned portions remains exposed to the action of the acid until the last of the scale is removed from other portions (65), and (2) that there is a skin effect causing brittleness, which becomes quite pronounced on thin specimens. This brittleness is generally presumed to be due to surface absorption of hydrogen (60, 61).

Experiments have been conducted at the bureau with a view to determining the conditions in the pickling operation that tend to increase brittleness (66a). The change in the resistance to alternating stresses for steel rods and in the Erichsen penetration test for steel sheet was used as a measure of the brittleness. The results indicated that pickling results in: (*a*) a permanent effect caused by the roughening of the surface and (*b*) a temporary effect, probably the result of hydrogen. The previous treatment of the steel, for example, cold working, determines the magnitude of the effect to a large extent. Increasing the temperature of the pickling bath, as well as prolonging the immersion period, increases the resulting brittleness. Upon standing, for example, three days, the pickled rods and sheets recovered their normal

properties. Two hours at 100° C. or 10 minutes at 150° C. was found sufficient to bring about almost complete recovery. Treatment of pickled specimens with oxidizing agents did not produce any measurable decrease in brittleness.

In the electrolytic method of pickling (62, 66) the sample is placed as cathode or anode in an electrolyte through which a current is passed. When the steel is the cathode, the hydrogen liberated thereby reduces some of the oxide scale and also aids mechanically in flaking off much of it; when the steel is the anode, the oxygen thereby liberated mechanically detaches the scale, which later may dissolve in the electrolyte. The concentration of hydrogen at the cathode would be expected to cause more brittleness, as compared with the anode, and experiments made elsewhere have shown that samples cleaned at the anode are much less brittle (61) than those cleaned at the cathode.

Of the mechanical methods of cleaning, the sand blast is the one most widely used. The strong stream of sand particles abrades or chips off the particles of scale from the steel. The method gives a smooth, bright surface, but takes more time than pickling and does not satisfactorily reach crevices. Steel shot and crushed steel are said to have some advantages over sand. It must be remembered that the "cold work" of impact will cause hardening of the surface, which may be quite noticeable on thin sections and sometimes quite harmful.

Another process of mechanical cleaning consists in tumbling the specimens in a rotating barrel with emery and water. It is an abrasion process. A similar method used on small articles involves rolling with emery and oil between rollers. It is the mildest process of mechanical cleaning, and although it is quite slow, it has advantages for springs and the like in that it avoids both the brittleness from pickling and the hardening from the sand blast.

V. METHODS OF TESTING COATINGS.

1. DESCRIPTION OF METHODS.

Considerable difference of opinion has been expressed concerning the relative merits of the different types of protective coatings, and various tests have been suggested to show the virtues of a particular coating. The basis on which some comparative tests are made is incorrect; for instance, the comparative values of lead, tin, or terneplate, and zinc can not be determined by treat-

ment with sulphuric-acid or ammonium-chloride solutions, as is sometimes suggested; the Preece test should not be applied to sherardized coatings and results obtained by this test on hot-dipped or plated coatings are not comparable. If the Preece test is made on the same type of material by the same operator under exactly the same conditions of time, temperature, concentration of solution, etc., comparable results may be obtained. There is no universal test that can be applied to the different kinds of protective coatings; each type must be considered alone, and the limitations of each must be taken into account.

The usual methods for testing zinc coatings are the Preece test (24), the hydrochloric acid-antimony chloride method (68), the basic lead-acetate method (71), and the salt-spray test (69), which recently has been receiving considerable attention. In addition to these purely chemical methods, metallographic measurements are also made of cross sections of the coating of the material under consideration.

(*a*) Stripping tests.—The Preece test is made by dipping, for a period of one minute each, the carefully cleaned sample in a solution of copper sulphate. The sample is washed in running water and lightly rubbed with clean waste between dips, and the appearance of bright adherent copper indicates the end of the test. The solution is prepared by dissolving 36 parts of commercial copper-sulphate crystals in 100 parts of water and then adding some cupric oxide to neutralize any free acid. This solution is diluted with water until its specific gravity is 1.186 at 18° C., and it should be used at approximately the same temperature.

The hydrochloric-acid antimony-chloride method for determining the amount of coating on galvanized metal is as follows:

A sufficient number of specimens should be used in each test to have an area of not less than 25 cm^2 (4 square inches). They are weighed (to the nearest milligram) and then dipped in 100 cm^3 (or more if necessary to cover the specimens) of concentrated hydrochloric acid (specific gravity 1.20), to each 100 cm^3 of which has been added 5 cm^3 of a solution made by dissolving 20 g of antimony trioxide in 1,000 cm^3 of concentrated hydrochloric acid. The same portion of hydrochloric acid may be used repeatedly up to five times by adding before each immersion an additional 5 cm^3 of the antimony-chloride solution. The samples are immersed in the solution for one minute. They are then washed and scrubbed in running water to remove the deposited anti-

mony, and are dried and reweighed. The loss in weight represents the weight of the zinc coating, which is calculated directly to grams per square decimeter; or to ounces per square foot by multiplying the grams per square decimeter by 0.328 (or for practical purposes, by dividing by 3). Often it may be most convenient, on irregular-shaped parts, to express the weight in grams (or milligrams) per piece, thereby avoiding uncertainty due to the area of a sample.

The basic lead acetate method is carried out essentially as follows:

The solution is prepared by dissolving 400 g of crystallized lead acetate in 1 liter of water, to which is then added 4 g. of powdered litharge. After shaking, the solution is decanted or filtered and is diluted until the specific gravity is 1.275 at 15.5° C. The weighed test specimens are immersed in a sufficient amount of this solution to cover them, and at the end of three minutes are removed and freed from adhering lead by rubbing or brushing lightly. They are again immersed for successive three-minute periods (usually four periods are sufficient), until a bright iron surface is exposed. The specimens are then cleaned, dried, and reweighed, the loss in weight representing the weight of the zinc coating.

(*b*) SALT SPRAY.—The operation of the salt-spray test has received considerable attention at the Bureau of Standards during the last two years, and although all types of protective coatings have been tested, special attention was given to zinc coatings.

The test as conducted at the bureau is made in an Alberene stone box, with a glass cover and glass supports for the samples (Fig. 17). The construction is indicated in the accompanying diagram. The stone box is inclined so that drops of solution collecting on the cover will run down to the edge instead of dripping on the samples.

A 20 per cent solution (by weight) of commercial sodium chloride (20 g salt and 80 cm^3 water, or 2 pounds salt and 1 gallon water) filtered if necessary, is used, and with an air pressure of about 6 or 7 pounds per square inch a very fine mist is produced.

The compressed air is passed through a glass-wool or cotton plug and then through water to remove oil and dust, and to saturate the air with water vapor which prevents concentration of the salt solution and crystallization of the salt on the tips of the atomizer. The baffle plate prevents the salt spray from blowing directly against the test pieces.

The samples, after being washed with gasoline and ether to remove all grease, are placed in the spray box in a vertical position on the glass rods or strips. They are removed from the bath every 24 hours, washed with water, using a moderately stiff bristle brush, and after drying are carefully examined for the presence of red or yellow iron rust. The first appearance of rust indicates the conclusion of the test, but valuable information may be obtained by continuing the test and observing the extent of the corrosion produced by longer exposure.

If Alberene stone is not available the box may be made of glass, stoneware, porcelain, waterproofed wood, or any other insoluble and noncorrodible material, and all connections should be of glass or rubber.

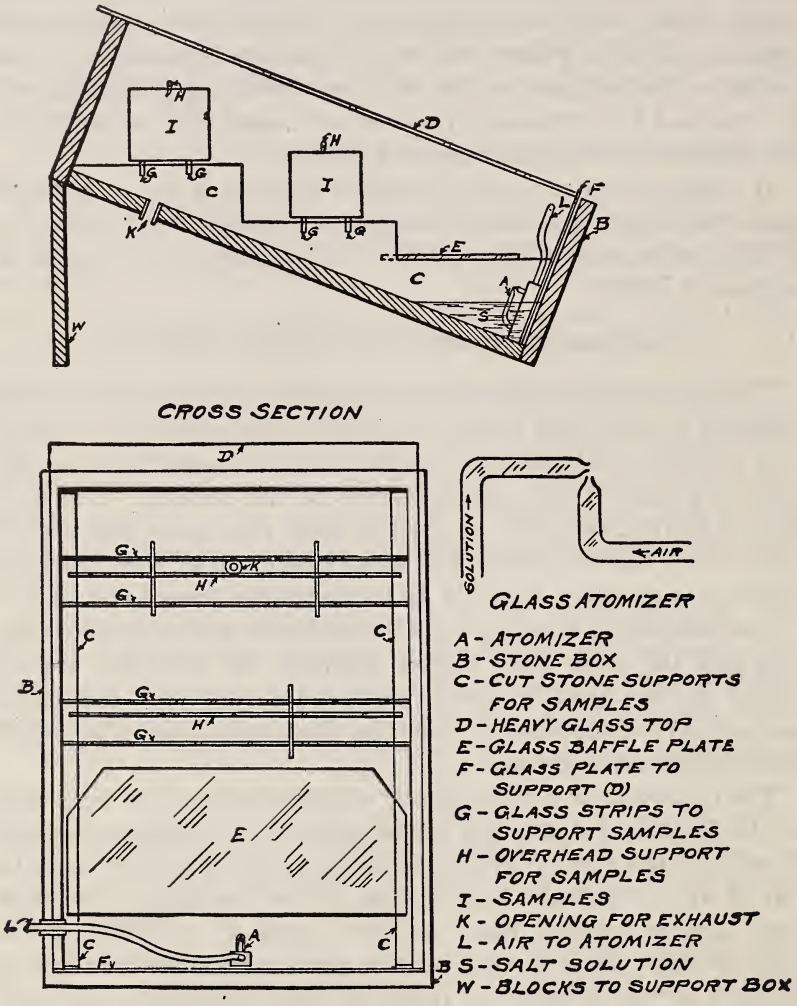
2. COMPARATIVE VALUES OF DIFFERENT METHODS.

The hydrochloric acid-antimony chloride and basic lead acetate methods are stripping tests and give the total amount of coating on a surface; the Preece test has been used to show thin spots and also, in a general way, the thickness of the coating. The lead-acetate method may also be used to show thin spots, but used in this way is liable to show the same irregularities that led committee A–5 of the A. S. T. M. to condemn the Preece test (75).

The comparative value of the hydrochloric acid-antimony chloride and the basic lead acetate methods for stripping are discussed in the report of committee A–5 for 1917 (75), and either method is considered satisfactory for sheet metal and wire, which were the materials tested.

The hydrochloric acid-antimony chloride method has been used at the Bureau of Standards almost entirely for stripping, because it removes the coating more quickly and can be applied to material of any shape and to all types of zinc coatings. The basic lead acetate method does not lend itself to irregular pieces, such as bolts, nuts, screws, etc., or parts with holes in them on account of the difficulty of removing the precipitated lead from the small depressions or holes and on account of the possible failure to react with sherardized coatings, which is also characteristic of the Preece test.

The hydrochloric acid-antimony chloride solution usually removes plated zinc completely in from 5 to 15 seconds and hot-dipped zinc in less than 30 seconds, but it has often been found that sherardized zinc is not completely removed during a 1-minute



SALT-SPRAY BOX FOR ACCELERATED CORROSION

FIG. 17.—*Salt-spray box for accelerated corrosion.*

immersion—four immersions sometimes being required to remove all the coating.

The following results illustrate the progressive loss of coating when four pieces of sherardized sheet metal, 1 inch square, were dipped in the hydrochloric acid-antimony chloride solution for periods of one minute each.

Dip.	A.	B.	C.	D.
	g.	g.	g.	g.
First	0.3371	0.4102	0.3966	0.8380
Second	.0490	.0158	.0171	.0477
Third	.0017	.0017	.0017	.0040
Fourth	.0010	.0008	.0010	.0007

The fourth value may be attributed to iron, as these figures are of the general magnitude of those obtained when bare iron is treated with the acid mixture used in stripping.

The following figures indicate that the acid method of stripping may be more accurate for electrolytic zinc than the basic lead-acetate method which was shown by accurately weighing the amount of zinc deposited on some iron sheets and then stripping them.

Method of stripping.	Weight of coating.		Coating found.
	Deposited.	Stripped.	
	g.	g.	Per cent.
Lead acetate	0.2888	0.2537	88
	.1694	.1572	93
Hydrochloric acid-antimony chloride	.2141	.2157	100.7
	.1965	.1992	101.4

The salt-spray test has been applied to a large number of samples, some of which were taken from stock at various plants, while other samples were prepared especially for this purpose. These tests were made in conjunction with stripping tests and metallographic examination. No definite conclusion as to the life of a coating determined by the salt-spray test, the amount of zinc determined by stripping, and the thickness of the coating measured metallographically could be drawn from the results obtained. The following examples taken from the large number tested illustrate the differences between amount of coating determined by the two methods and the variation shown by the salt-spray test.

Sample.	Thickness of coating (by stripping).	Microscopic examination of cross sections.	
		Average.	Average minimum.
	Inch.	Inch.	Inch.
A (hot dipped)	0.00276	0.00303	0.00173
	.00307	.00646	.00339
B (hot dipped)	.00191	.0028	.00233
	.00185	.0046	.00268
C (hot dipped)	.00181	.0039	.00260
	.00172	.0029	.00189

Salt-Spray Test.

Type of coating.	Thickness of coating (by stripping).	Number of 24-hour days required for first appearance of rust.
	Inch.	
Electroplated	0.0004	3
Do	.00077	15
Do	.00073	9
Hot dipped	.00109	5
Do	.00133	6

The tests from which the above conclusions were drawn were repeated to see if more consistent results could be obtained, but no better agreement was found. It was thought these differences might be due either to the manipulation of the salt-spray test, to the very irregular shapes of the test pieces, or to a lack of uniformity in different samples of the same kind from the same lot. It was found on investigation that samples of plated and hot-dipped sheets and chilled cast zinc placed in the salt-spray tank in a vertical position corroded more rapidly than those in a horizontal or an inclined position. It was also found that zinc is not removed by immersion in a solution of salt nearly as rapidly as it is by a spray of the same solution, and consequently zinc in the holes or depressions in the surface of a specimen where the salt solution may collect will not be removed as rapidly as at other places. It becomes evident that although the thickness of plated zinc on recessed parts is less than on outer surfaces, they may not show failure as rapidly as the outer surfaces. It was also found that the amount and distribution of zinc on different samples of sheet metal, prepared at the same time and presumably under similar conditions, varied so much that the results obtained on one of several samples could not be taken as characteristic of the set.

A hard and adherent coat of basic zinc carbonate nearly always forms on the surface of the test piece when exposed to the action of the salt spray, and efforts to remove this completely without affecting the metalic zinc have not been successful. Treatment with acids undoubtedly removes zinc, although Tambou (74) recommends a mixture of ammonium carbonate, ammonium chloride, and ammonia for differentiating between zinc oxide and metallic zinc. This solution was not found satisfactory, as it attacks metallic zinc somewhat readily. A zinc-plated sheet (51.7 cm^2) immersed for periods of 15 minutes each in a solution lost weight as follows:

	mg
First dip	6.4
Second dip	3.6
Third dip	4.1
Fourth dip	4.2

After trials of various methods to remove the basic zinc carbonate the one finally adopted is to brush the sample daily in running water with a moderately stiff bristle brush. This was found to have practically no effect on metallic zinc, but it did not remove all the zinc salts. This layer must have some protective action, and as it is not uniformly distributed, zinc will be removed more rapidly at some places than at others, producing erratic results.

The salt-spray test as a measure of the relative value of zinc coatings depends on the time required for the complete removal of the zinc at the thinnest points, which is usually indicated by the appearance of iron rust. It was thought that iron exposed to the action of the salt fog would show rust almost at once, but this is not always true. Numerous cases have been observed, however, in which areas of iron as large as 1 cm^2 have been completely freed from zinc, as shown metallographically, yet no rust appeared. This is probably due somewhat to the type of iron exposed, and also to the protective action of the adjacent zinc through the strong salt solution as electrolyte, for it can readily be shown that certain steels corrode more readily than others, and that the zone of protection exerted by zinc on iron increases readily with the concentration of the salt solution. It is difficult to explain the quick appearance of iron rust on zinc-coated material in the salt-spray test unless it is assumed that there is an insufficient layer of salt solution between the zinc and exposed iron to allow the zinc to exert its electronegative nature, or that the basic zinc

carbonate which is formed collects in such a way that it insulates the zinc from the iron and destroys its protective effect.

Although the salt-spray test is subject to many objections, it may be regarded as the best test for zinc coatings that has yet been developed. It is especially useful in determining the relative value of zinc coatings for marine exposure. No definite statement can be made about the life of zinc coating in this test, but in general a sample showing rust spots in less than one day (24 hours) should be regarded as unsatisfactory, while a life of two or three days would indicate a coating that could safely be used under moderate conditions of exposure, and a life of at least four to six days should be required for severe conditions of exposure.

Since electropositive coatings accelerate the corrosion of iron at exposed points, continuity of coating is of more importance than the thickness of the protecting layer. Any test which will effectively show the presence, number, and approximate size of breaks or pinholes may be used to indicate in a general way the quality of the coat as applied. The salt-spray test will detect pinholes in a comparatively short time (usually from 3 to 10 hours), and on longer exposure give some indication of the probable life of the protective coating. But the comparative value of the various metals can not be determined by this method alone; purpose and service conditions also must be taken into consideration.

Other tests which detect lack of continuity in metal coats have the advantage of speed, while their application does not spoil the part tested for subsequent use. Such tests are based upon color reactions which take place between the solution and exposed (uncoated) iron. Pinholes in most electropositive coatings can be detected readily by immersing the sample in a 1 per cent solution of sodium ferricyanide in 2 per cent sulphuric acid. The appearance of a blue precipitate at any point indicates a hole in the coating, or exposed iron. This test is readily applied to the electropositive coatings such as lead, copper, lead-tin, or lead-antimony alloys. Acetic acid may be substituted for sulphuric acid, but the action will be slower. Similar results may be obtained by exposing to the air a specimen which has been dipped first in dilute acetic acid and then in a warm solution containing 5 per cent tannin and 1 or 2 per cent hydrogen peroxide. Breaks in the coatings are indicated by a blue precipitate.

The oxide coatings can not be tested by any method so far developed, because the iron in the coating gives the same results as the base metal itself, and their protective value depends often on the amount of oil in the coating.

The phosphate coatings are more readily tested, but in this case, too, the iron in the coating makes it difficult to draw definite conclusions. A great many tests have been made at this bureau on samples prepared by treatment with the various phosphoric-acid solutions, and it can be definitely stated that this treatment does not give satisfactory protection for steel parts that are exposed to water, salt air, moist atmosphere, or considerable friction, but it has some merit if conditions of exposure and handling are very moderate. The value of this treatment is increased if the treated surfaces can be frequently oiled, but this will not materially increase its resistance to mechanical action. The experience of this bureau indicates that this treatment has not been successfully applied to casehardened products without removing most, if not all, of the hardened surface by sand blasting or pickling.

VI. RECOMMENDATIONS CONCERNING COATINGS.

1. Zinc coatings should be given preference over all others when the object of the coating is protection against corrosion only.

2. For general use on large, smooth surfaces, sheets, rods, wires, pipes, etc., the hot-dipped zinc coatings are entirely satisfactory, although some of the other processes are more economical in the amount of zinc used. On articles which must be sharply bent or shaped too heavy coatings of this hot-dipped type should not be used on account of the tendency of the coating to flake off at such points.

3. One ounce of zinc per square foot of surface exposed (0.0017 inch thickness) may be considered as satisfactory for most purposes, but less may be sufficient if evenly distributed.

4. Of the different types of zinc coatings the hot dipped and sherardized are not to be recommended for hardened and tempered steels (springs, etc.); the plated zinc and the sherardized coatings are both recommended for accurately machined parts; the "spray" coatings are valuable for large or complex parts which must be coated in situ or after assembling.

5. For indoor and to a limited extent outdoor use, for parts which are so placed as to be easily inspected and which are kept

well oiled, other coatings than zinc (e. g., the oxide and other black finishes) may be used. For severe service zinc only should be depended upon.

6. In general, nothing is gained, from the standpoint of resistance to corrosion, by first coating an article with copper, or a similar metal, and then finishing with zinc. If a zinc coating is to have a black finish, black nickel may be used as a finish.

7. The use of oil, and like substances, on any type of coating is to be strongly recommended. The life of zinc coatings, particularly those of a porous character, may be prolonged almost indefinitely by periodically oiling them.

8. The time required for the appearance of rust on zinc-coated articles when exposed to salt spray may in a general way be taken as an indication of whether or not the coating is satisfactory for outdoor exposure, e. g.: 24 hours, unsatisfactory; 48 to 72 hours, satisfactory for mild exposure; and 96 to 144 hours, satisfactory for severe exposure.

Appendix.—SELECTED BIBLIOGRAPHY.

The bibliography of the general subject of corrosion is extremely voluminous; probably more articles have been written on this subject than on any other phase of metallurgy. Many of these merely reiterate statements which have previously been published. Below is given a list of the most helpful contributions to the discussion of different phases of the subject as related to the rust-proofing of iron and steel by means of metallic coatings. The references to the literature throughout the text have been made by referring to the proper number in the first column.

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